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X-ray Diffraction Evidence for Transition Metal Cation Exchange in Anionic Clays in Room-Temperature Aqueous Fluids

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Beamline(s): X7B

Introduction: In anionic clays, trivalent cations within brucite-like octahedral sheets generate a net positive charge that is electrostatically balanced by anionic groups in the interlayer region. Over the past decade, scientists have explored the potential of anionic clays for environmental remediation, particularly focusing on the heightened ability of these materials to swap their interlayer anions with negatively charged species in solution, such as pesticides, humic acids, cyanide ions, and radioactive wastes. Recently, Komarneni et al. (1998) made a novel and surprising observation that hydrotalcite-like anionic clays can remove significant amounts of dissolved transition metal *cations* in solution, such as Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}, at room temperature. Based on their measurements of changes in fluid chemistry, these authors argued for a direct exchange between the structural Mg cations that compose the octahedral sheets and the transition metals in solution.

Methods and Materials: We have examined the reaction products of hydrotalcite-like clays in the presence of dissolved transition metals using synchrotron X-ray powder diffraction, and our Rietveld analyses support the proposed exchange model. Commercially prepared manasseite $\{[Mg_6^{2+} Al_2^{3+} (OH)_{16}]^{2+} \cdot [CO_3 \cdot 4H_2O]^{2-}\}$ powders (0.05 gm) were equilibrated at room temperature in 25 ml solutions containing 0.01 M of $CuCl_2$ and, separately, $ZnCl_2$ for 24 hr at room temperature at pH 4-5. Synchrotron X-ray diffraction data for the dried powders were collected at Beamline X7B, National Synchrotron Light Source, Brookhaven National Labs using a Mar345 imaging plate.

Results: Rietveld analyses of the starting and reacted powders were well-behaved with final weighted residuals below 4.0. The Cu-exchanged manasseite revealed a significant amount (57%) of reaction product as paratacamite $[Cu_2Cl(OH)_3]$ with minor quantities of periclase. Occupancy factors for the octahedral sites in the cuprous manasseite refined to 31% Cu and 69% Mg. Similarly, the Zn-exchanged manasseite yielded minor amounts of brucite, periclase, and zincite, and octahedral occupancy factors for manasseite were 21% Zn and 79% Mg.

Our analyses also have offered the first high-resolution structure refinement for end member manasseite with a = 3.0534(1) Å and c = 22.964(2) Å in space group $R\bar{3}m$ (R_{wp} = 2.85). Moreover, our temperature-resolved synchrotron heating experiments revealed that Cu-substituted manasseite exhibits a thermal stability that is very similar to the end-member composition, with both structures transforming reconstructively at ~150˚C.

References: S. Komarneni, N. Kozai, and R. Roy "Novel function for anionic clays: selective transition metal cation uptake by diadochy," *Journal of Materials Chemistry*, *6*, p. 1329-1331 (1998)